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Databases searched:

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Other: Online - WPI, EPODOC, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	GB 2307912 A (Armstrong)	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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(71) Applicant(s)

Armstrong World Industries Inc

(Incorporated in USA - Pennsylvania)

P O Box 3001, Liberty & Charlotte Streets, Lancaster,
Pennsylvania 17604, United States of America

(72) Inventor(s)

Angela S Rosenberry

Claude R Rupp

Songvit Setthachayanon

(74) Agent and/or Address for Service

Abel & Imray

Northumberland House, 303-306 High Holborn,
LONDON, WC1V 7LH, United Kingdom

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R32J9E R32J9G R32KL R32T2X

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(54) Polyurethane (meth)acrylate coating compositions

(57) Floor coverings include a wear layer made from a coating composition including a multifunctional polyurethane(meth)acrylate oligomer. The multifunctional polyurethane is made by reacting a polyisocyanate with a functionality equal to or higher than 3, a polyester polyol, and a hydroxyalkyl-(meth)acrylate with a molecular weight of about 116 to about 600. The coating composition preferably includes a reactive (meth)acrylate diluent and a photoinitiator.

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COATING COMPOSITIONS

The present invention relates to coating compositions and floor coverings made with the coating compositions, and more particularly, to radiation-curable coatings which have superior gloss retention, and abrasion, gouge and stain resistant surfaces.

Coatings which provide wear layers on floor coverings are designed to provide durability and cleanability to the flooring materials. Durability in this case refers to the ability of the coatings to resist wear and tear. The wear and tear come in two forms:

(a) abrasion in micro scales at the very top of the surface that results in changes of gloss and appearance, and (b) deep scratch and gouge damage from soil or other grit particles dragged under foot traffic. Cleanability refers to the ability of the coatings to resist stain and chemical attacks, and maintain their original appearance.

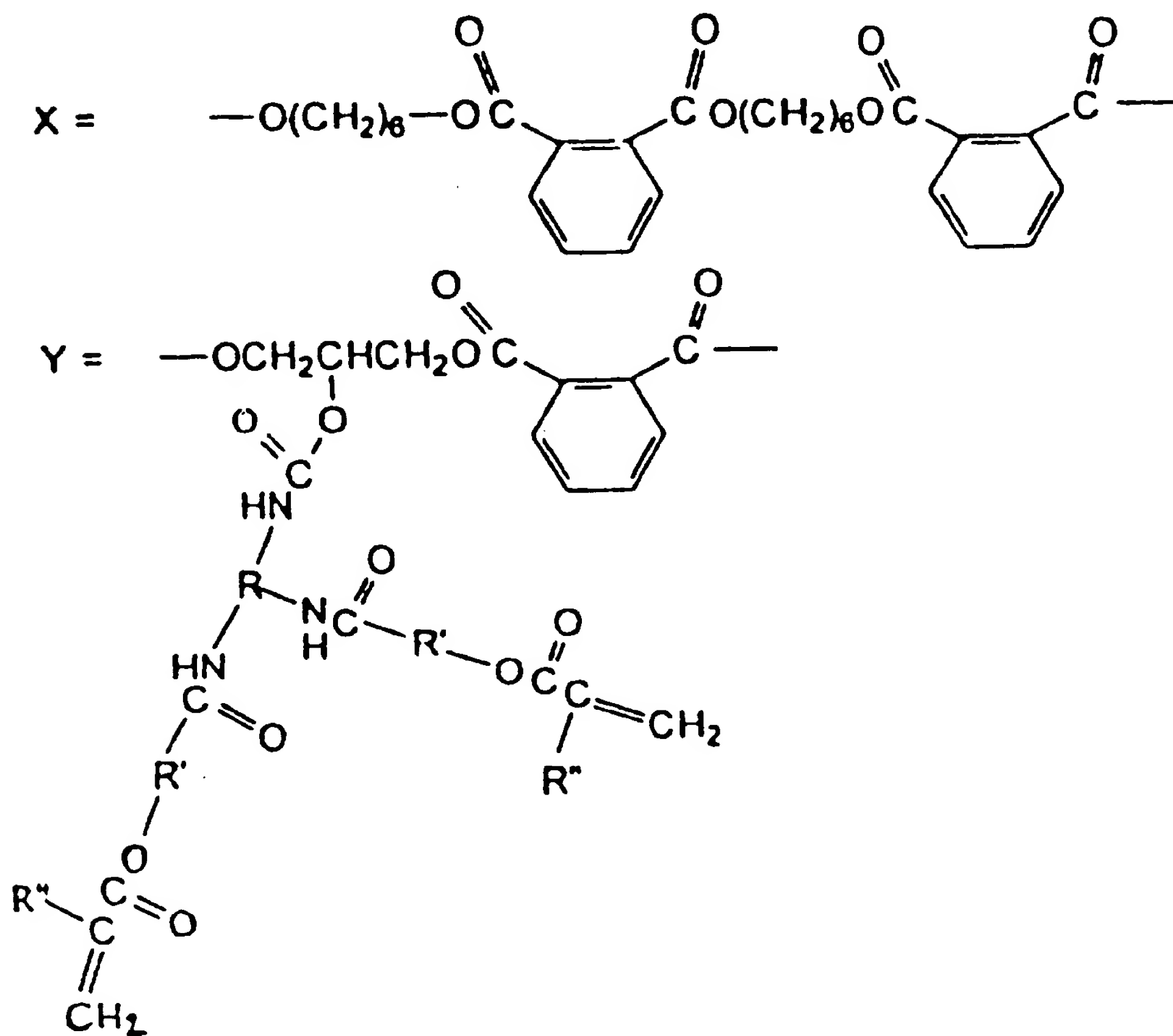
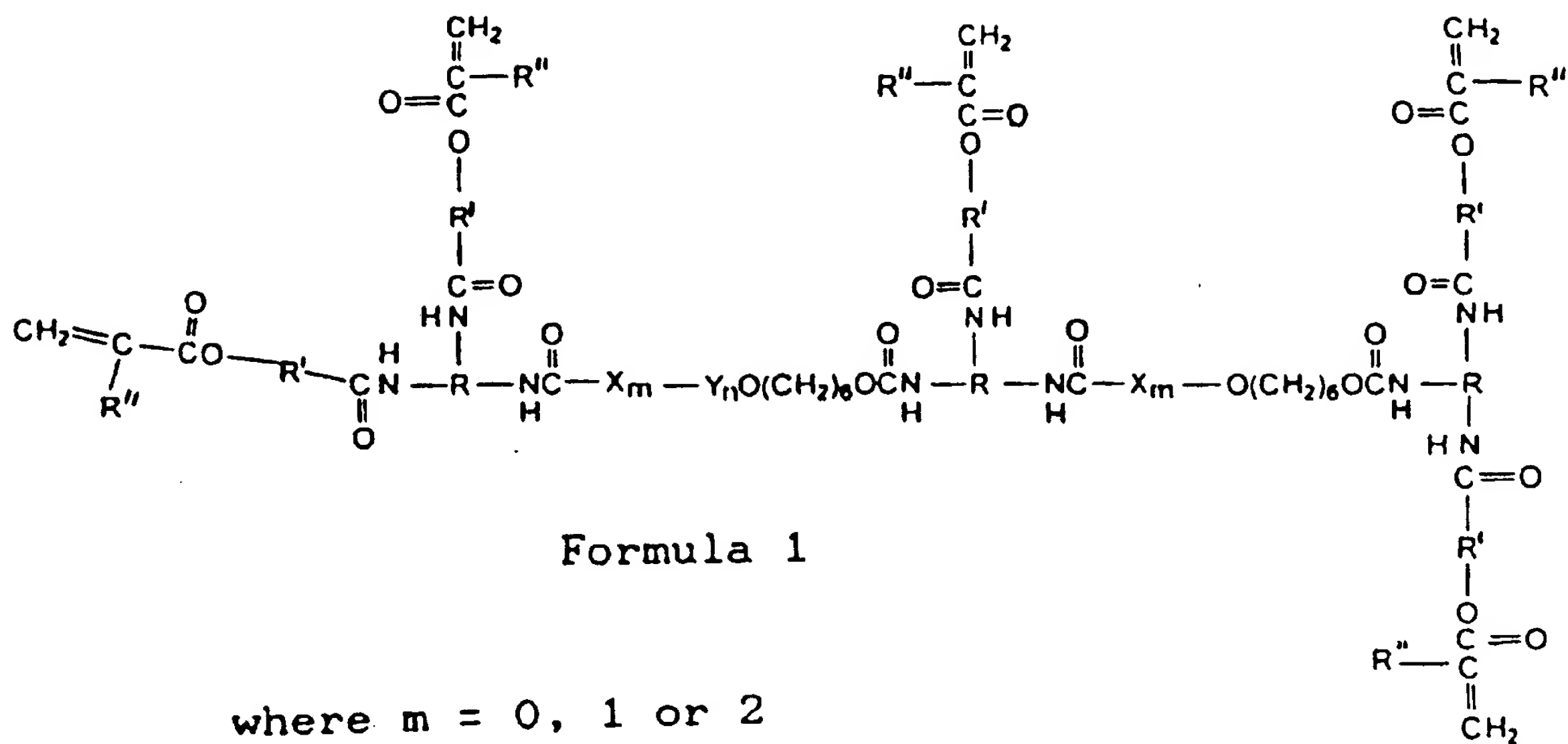
Previously proposed polyurethane-based wear layer compositions provide either gloss retention, stain resistance or gouge resistance, but none of them has all three properties. Consequently, the need exists for high performance coatings which have the aforementioned gloss retention, stain, abrasion and gouge resistance for floor coverings.

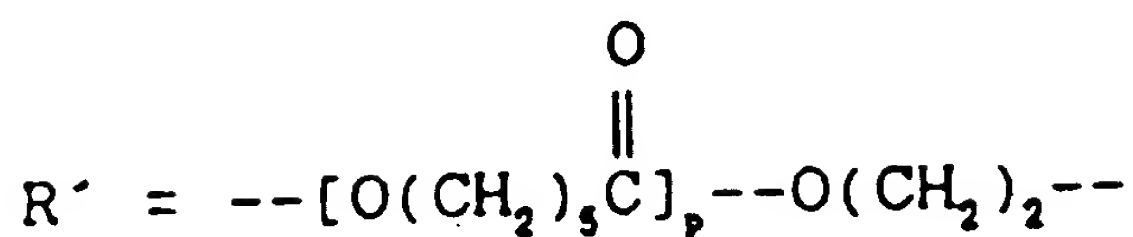
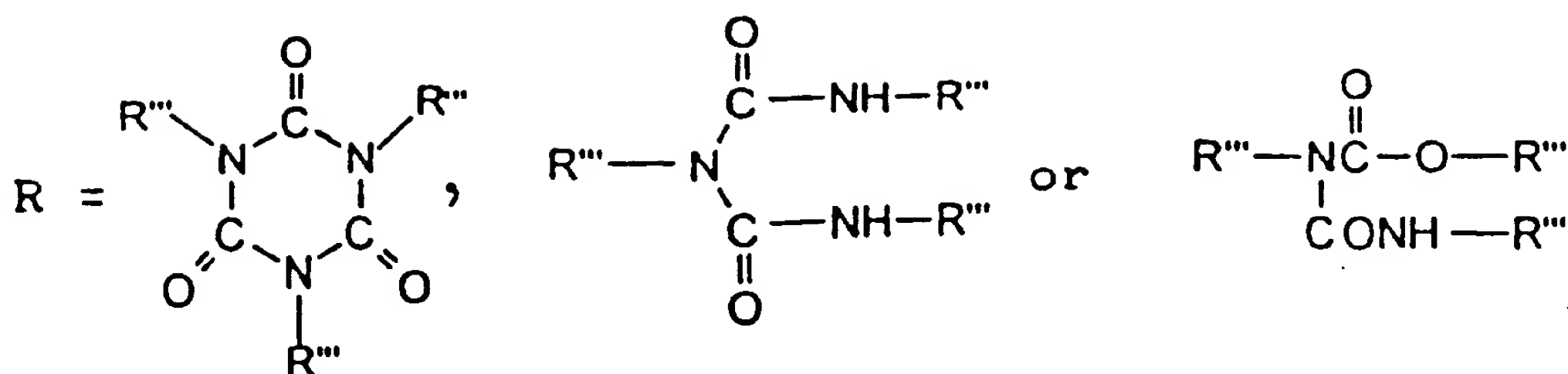
The present invention provides a coating composition comprising a compound comprising structural units

derivable, and preferably derived, from a polyisocyanate having at least two, for example, at least three, isocyanate functionalities per molecule, structural units derivable, and preferably derived, from a polyester polyol, and structural units derivable, and preferably derived, from a hydroxyalkyl(meth)acrylate having a molecular weight of about 116 to about 600.

The present invention also provides a coating composition comprising the reaction product of a polyisocyanate having three to six isocyanate functionalities per molecule, an aromatic polyester polyol and a hydroxyalkyl(meth)acrylate with an average molecular weight of about 344 to about 472 and, preferably, a (meth)acrylate reactive diluent which preferably has a molecular weight of at least 200 and less than 2000.

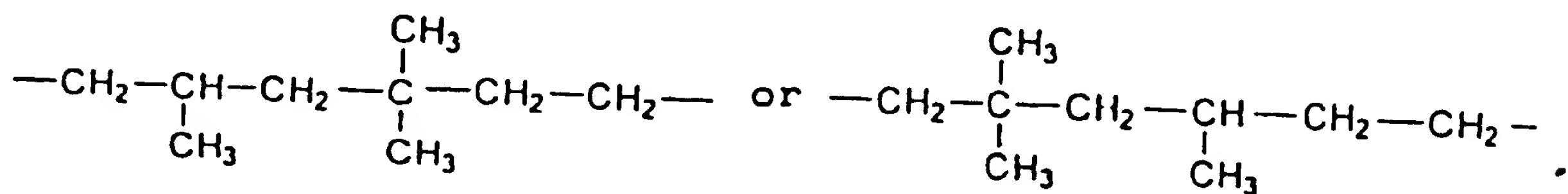
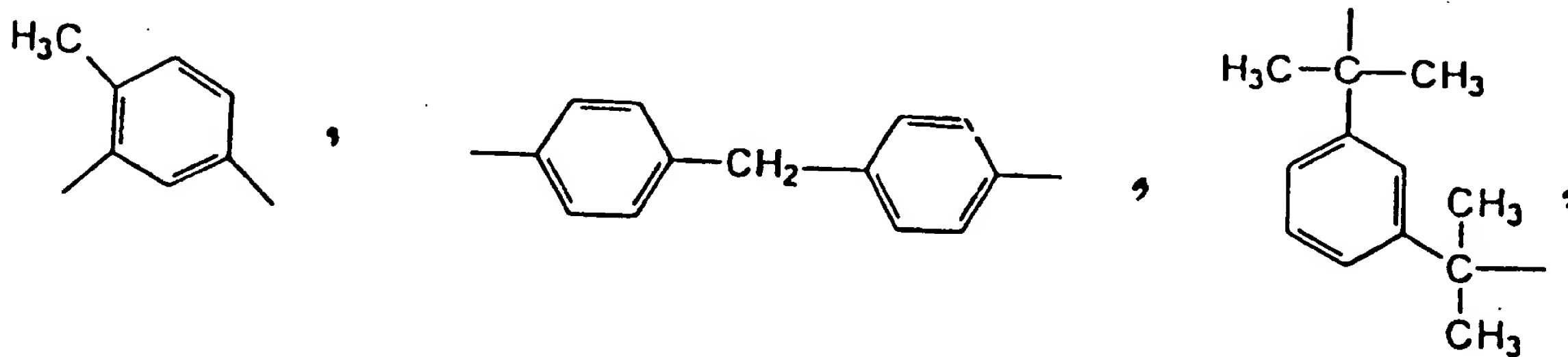
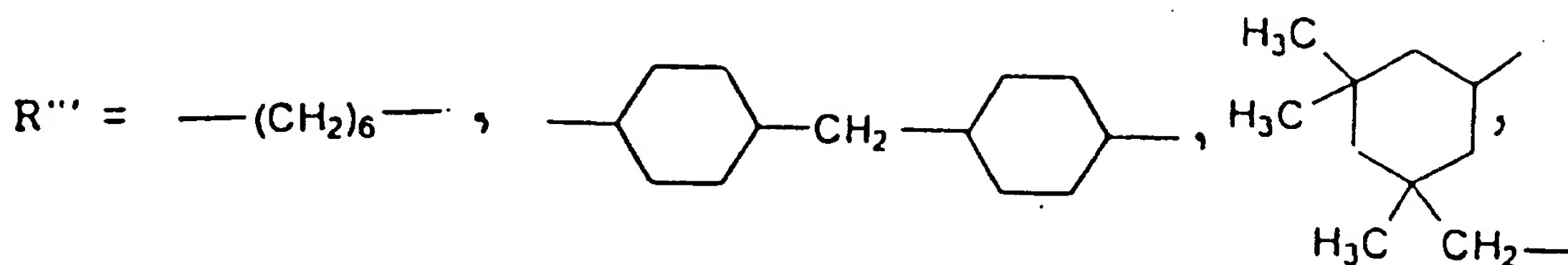
The invention further provides a coating composition comprising a multifunctional polyurethane(meth)acrylate and, preferably, a (meth)acrylate reactive diluent which preferably has molecular weight of about 200 to about 2000, the multifunctional polyurethane(meth)acrylate having the structure given in Formula 1 below:





$p = 1, 2 \text{ or } 3$

$R'' = \text{H or CH}_3$



Where the formulae given above contain more than one group represented by the same symbol, those groups may be the same or different.

The invention also provides a method of manufacturing a floor covering, or other coated substrate, which comprises applying to a base layer a composition according to the invention, and curing the coating, and coated substrates made by the method.

The invention further provides a floor covering comprising a base layer and wear layer adhered to the base layer, the wear layer comprising a cured coating composition, the coating composition preferably comprising a (meth)acrylate reactive diluent which preferably has a molecular weight of about 200 to about 2000 and the reaction product of a polyisocyanate with a functionality of 3 to 6 isocyanate functionalities per molecule, a polyester polyol, and a hydroxyalkyl(meth)acrylate which preferably has a molecular weight of about 344 to about 472.

The reaction product, which is an oliger, is preferably the reaction product of a polyisocyanate with a functionality equal to or higher than 3, preferably equal to or higher than 3.5, a polyester, especially an aromatic polyester polyol, preferably a phthalate polyester polyol, and a hydroxyalkyl(meth)acrylate with a molecular weight of about 116 to about 600, especially about 344 to about 472. The resulting oligomer is liquid

at room temperature, highly branched, and has multi(meth)acrylate functionality. As used herein, the term "(meth)acrylate" and its variants mean "acrylate, methacrylate and mixtures thereof".

The coating composition may consist essentially of the oligomer. However, the oligomer without a diluent is viscous and difficult to apply. Therefore the coating composition of the present invention preferably includes a diluent. The preferred diluent is a reactive (meth)acrylate diluent.

The coating composition may be cured, for example, by electron beam curing or UV curing. The preferred composition includes a photoinitiator and the composition is cured using both an electron beam and UV light.

It is known that abrasion resistant and non-yellowing coatings can be obtained from radiation-curable polyurethane (meth)acrylate based on aliphatic diisocyanates such as isophorone diisocyanate (IPDI) or methylene-bis(4-cyclohexylisocyanate) (Bayer Corporation's Desmodur W). However, higher functionality polyisocyanates such as isocyanurate, biuret and allophanate have not been used in radiation-cured coatings, nor are such uses disclosed in the prior art.

Because of their high reactivity, two-component coating systems must be mixed just prior to application. After the two components are brought together, there is a limited pot-life in which the mixture must be used before

it is rendered useless.

The present applicants have discovered that reacting, for example, isocyanurate trimers such as Bayer's Desmodur N3300 or biurets such as Bayer's Desmodur N100 or N3200 with a long chain hydroxyalkyl(meth)acrylate and a polyester polyol can produce one-component radiation-curable oligomers which have a long shelf-life. (Desmodur N3300 is an isocyanate trimer having an equivalent weight of 195; Desmodur N100 is a biuret isocyanate, having an equivalent weight of 191, derived from hexamethylene diisocyanate; and Desmodur N3200 is a biuret isocyanate, having an equivalent weight of 181, derived from hexamethylene diisocyanate.) The oligomers can give radiation-curable coatings of superior stain resistance, gloss retention, and abrasion and gouge resistance.

Preferred oligomers are prepared by reacting about 0.7 to 1.5 equivalents of Desmodur N-3300 with 1.0 equivalent of a mixture of hydroxyalkyl(meth)acrylate and phthalate polyester polyols (equivalent ratio of hydroxyalkyl(meth)acrylate to polyester polyol greater than about 0.10) to produce a highly branched, multifunctional (meth)acrylate polyurethane product. The product can be mixed with an acrylate reactive diluent and a photoinitiator to form a coating composition. Especially valuable properties are obtained when substantial quantities of high molecular weight

ethoxylated and propoxylated tri(meth)acrylates are the principle reactive diluents.

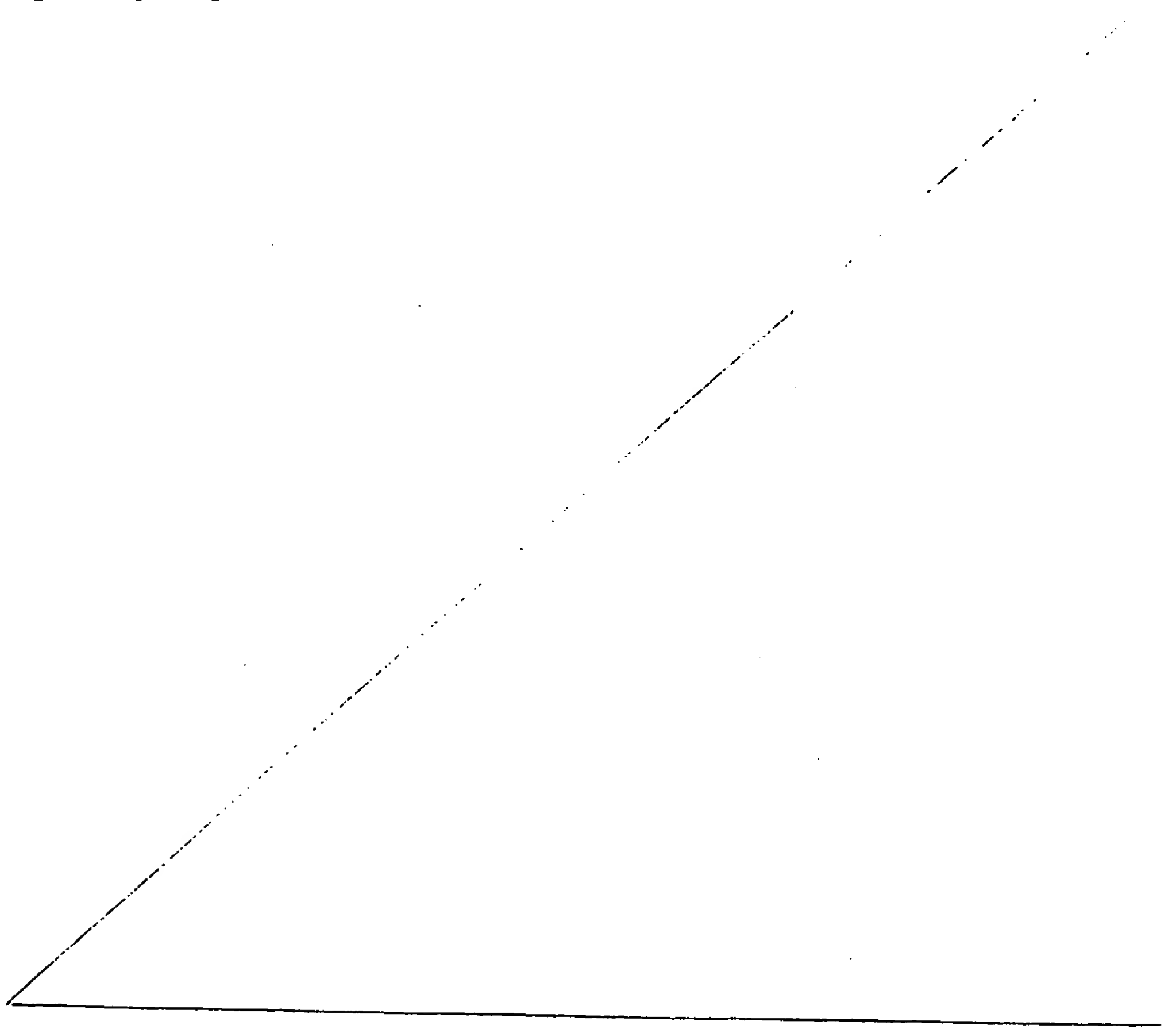
The aromatic polyester polyol is advantageously a polyester polyol of acid number of less than about 15, preferably less than about 5, comprising the reaction product of an equivalent excess of one or more polyols of equivalent weight less than 150 with at least one polycarboxylic acid or a derivative thereof, for example, an ester or anhydride thereof, at least 50 equivalent percent of the acid/derivative being selected from aromatic polycarboxylic acids and derivatives thereof. If the polycarboxylic acid is a phthalic acid/derivative, the result is a phthalate polyester polyol. Preferably at least 50 equivalent percent of the polycarboxylic acid/derivative is isophthalic acid, phthalic acid, terephthalic acid, phthalic anhydride, or dimethyl terephthalate.

The preferred multifunctional polyurethane (meth)acrylate of the present invention can be represented by Formula 1 given above, in which the various symbols have the meanings given above.

The isocyanurates, biurets and allophanates used according to the present invention can be aliphatic, cycloaliphatic or aromatic, for example, those prepared from 1,6-hexamethylene diisocyanate (Desmodur H); methylene-bis(4-cyclohexylisocyanate); 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane; 2,2,4-

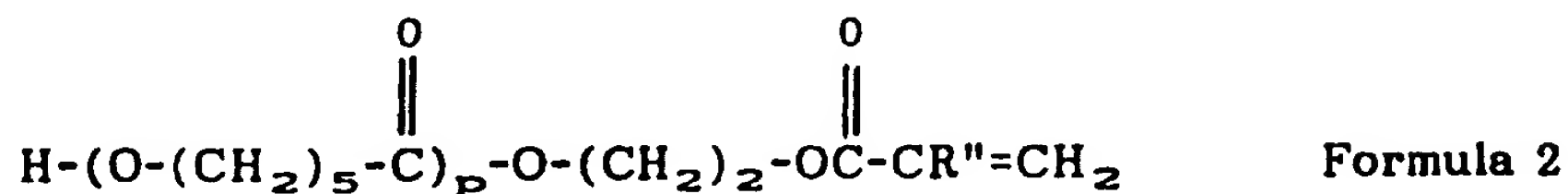
trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; toluene diisocyanate; methylenediphenyl diisocyanate; and tetramethylxylene diisocyanate. The preferred polyisocyanates are the trimer isocyanates represented by R in Formula 1 (isocyanurate, biuret and allophanate). The most preferred trimers are those derived from 1,6-hexamethylene diisocyanate which is commercially available as Desmodur N from Bayer Corporation.

Suitable hydroxyalkyl(meth)acrylates are hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, —



hydroxybutyl(meth)acrylate, hydroxyethylcarboxyethyl (meth)acrylate, and the polycaprolactone-based hydroxy(meth)acrylate .

in Formula 2:



where $R'' = \text{H}$ or CH_3 , and

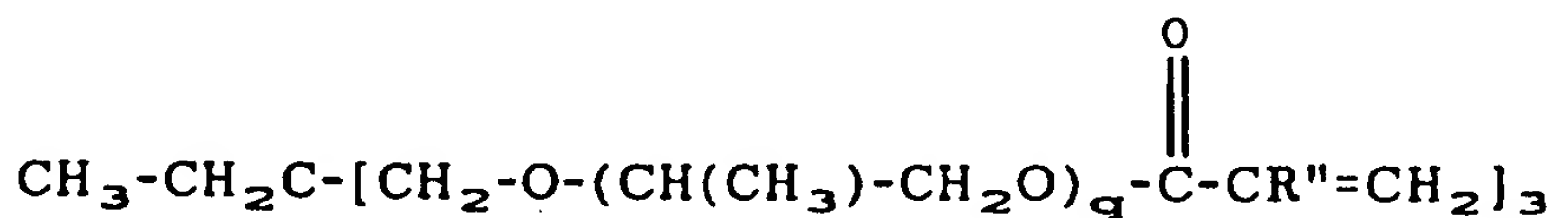
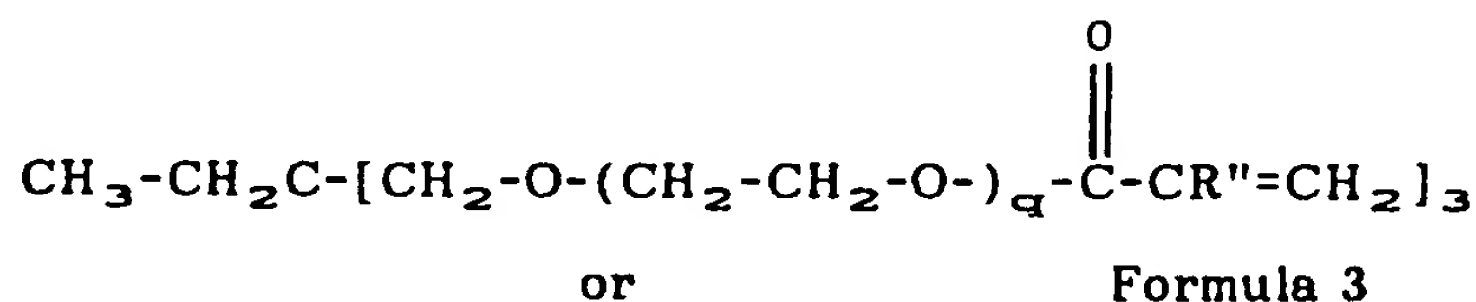
$p = 1, 2$ or 3 .

Polycaprolactone based hydroxy(meth)acrylates are supplied commercially by Union Carbide as Tone M-100 (molecular weight of about 344) and by San Esters Corporation as Placel FA and FM series (molecular weights from about 230 to about 472).

A preferred oligomer is prepared from Desmodur N-3300, Tone M-100 and a predominantly 1,6-hexylene phthalate polyester polyol. A predominantly 1,6-hexylene phthalate polyester polyol is defined as a phthalate polyester polyol wherein at least 50 equivalent percent of the <150 equivalent weight (eq. wt.) polyol is 1,6-hexanediol and wherein at least 50 equivalent percent of the polycarboxylic acid is phthalic acid or phthalic anhydride.

Phthalate polyester polyols suitable for the present invention can be prepared by a procedure similar to example 1 of US Pat. No. 4,138,299 by reacting acids such as isophthalic, terephthalic, phthalic (or phthalic anhydride), adipic, azelaic, and/or sebacic with polyols such as 1,6-hexanediol; trimethylol propane; triethylene glycol; neopentyl glycol; cyclohexane dimethanol; 2-methyl-1,3-propanediol; trihydroxyethylisocyanurate; and glycerol in the presence of a catalyst such as dibutyltin bislauryl mercaptide or stannous oxalate .

Suitable (meth)acrylate reactive diluents include (meth)acrylic acid, isodecyl (meth)acrylate, N-vinyl formamide, isobornyl (meth)acrylate, tetraethylene glycol (meth)acrylate, tripropylene glycol (meth)acrylate, hexanediol di(meth)acrylate, ethoxylate bisphenol-A di(meth)acrylate, ethoxylated neopentyl glycol di(meth)acrylate, propoxylated neopentyl glycol di(meth)acrylate, ethoxylated tripropylene glycol di(meth)acrylate, glyceryl propoxylated tri(meth)acrylate, tris (2-hydroxy ethyl) isocyanurate tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dimethylol propane tri(meth)acrylate dipentaerythritol monohydroxypenta(meth)acrylate, and trimethylol propane tri(meth)acrylate and its ethoxylated and propoxylated analogues of the structures given in Formula 3:



where $R'' = \text{H, or CH}_3$, and

$$q = 0, 1, 2, \dots, 9 \text{ or } 10.$$

The preferred (meth)acrylate reactive diluents are multifunctional acrylates with molecular weights of about 200 to about 2000. Examples of such are tetraethylene glycol diacrylate with a molecular weight of about 302, ethoxylated bisphenol-A diacrylate with a molecular weight of about 776 (SR602 from Sartomer Company), trihydroxyethyl isocyanurate triacrylate with molecular weight of about 423 (SR368 from Sartomer), trimethylol propane triacrylate with a molecular weight of about 296 (SR351 from Sartomer), and ethoxylated trimethylol propane triacrylates with molecular weights from about 400 to about 2000 (SR454, SR499, SR502,

SR9035, and SR 415 from Sartomer Company and Photomer 4155 and Photomer 4158 from Henkel Corporation).

To practice the present invention, it is preferred to employ photoinitiators by themselves or in combinations and/or in combination with photoactivators and photosensitizers. Suitable photoinitiators include benzophenone; 4-methylbenzophenone; benzyl dimethyl ketal; diethoxy acetophenone; benzoin ethers; thioxanthenes; 1-hydroxycyclohexyl phenyl ketone (Irgacure 184 from Ciba Corp); 2-hydroxy-2-methyl-1-phenol-propane-1-one; 4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-methylpropyl) ketone; 2,4,6-trimethylbenzoyl diphenylphosphine oxide; bis (2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide; 2,2-dimethoxy-2-phenyl acetophenone; 2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone; and 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one. A preferred photoinitiator is benzophenone, which may be used in conjunction with other photoinitiators, photoactivators and/or photosensitizers. A preferred combination is about two parts benzophenone per one part of 1-hydroxycyclohexyl phenyl ketone.

In addition, other components which may be useful can also be included in the present invention. These include flow additives, free radical inhibitors, thermal stabilizers, light stabilizers, dyes, pigments, optical brighteners, flatting agents, plasticizers, and others.

In preparing the oligomer of the present invention, a catalyst, e.g., dibutyltin dilaurate may or may not be included to aid the urethane formation between the polyisocyanate and the hydroxy-containing components. However, it is advantageous to prepare the oligomer in a clean vessel free of moisture or water. The vessel is equipped with dry-air blanket and a heating jacket, and has continuous mixing. It is further

advantageous to prepare the oligomer in the presence of substantial amounts of reactive acrylate diluent to help control heat of reaction which may otherwise cause undesired side reactions. The reaction temperature is preferably maintained at about 75°C to about 85°C. Higher temperatures can initiate undesired free radical polymerization. On the other hand, lower temperatures will retard or slow down the NCO/OH reaction.

The compositions of the present invention can be applied by, e.g., brushing, roller, gravure, spin, flow, or curtain coating at room temperature to an elevated temperature of up to about 75°C. The composition of the present invention has an excellent high temperature stability. Prolonged exposure to elevated temperature does not have any adverse effect on its superior properties. Radiation curing may be effected with ultraviolet or electron beam radiation. Although no photoinitiator is required when the composition is cured by electron beam, including a photoinitiator can further enhance the properties of coatings in accordance with the present invention.

The invention further provides a compound or reaction product as specified herein in connection with the compositions of the invention.

The invention also provides a method of making a compound or reaction product, which comprises reacting together a polyisocyanate having at least two isocyanate

functionalities per molecule, a polyester polyol, and a hydroxyalkyl(meth)acrylate having a molecular weight of about 116 to about 600 and further provides the product of such a method. In the method, one or more of the starting materials may be as specified herein in connection with the compositions of the invention.

The following Examples illustrate the invention.

Table 1

Polyols Used in the Following Illustrative Examples

5	Polyol 1:	hydroxyl number = 185, acid number < 0.5 prepared from: 20.0 equivalents of phthalate anhydride 23.8 equivalents of 1,6- hexanediol 6.0 equivalents of glycerine
10	Polyol 2:	hydroxyl number = 115, acid number < 0.6 prepared from: 20.0 equivalents of phthalate anhydride 25.75 equivalents of 1,6- hexanediol
15	Polyol 3:	hydroxyl number = 315, acid number < 0.6 prepared from: 20.0 equivalents of adipic acid 16.0 equivalents of trimethyl propane 20.0 equivalents of neopentyl glycol
20		

Example 1

	1. SR351 reactive diluent	16 parts
	2. SR499 reactive diluent	10 parts
	3. SR502 reactive diluent	10 parts
25	4. Tone M-100, hydroxyacrylate from Union Carbide	32.58 parts
	5. Polyol 1, hydroxyl equivalent weight (eq. wt.) of 303	8.87 parts
30	6. Desmodur N3300, Bayer's isocyanurate trimer eq. wt. of 195	22.55 parts

The above ingredients were mixed in a clean and dry vessel, heated, with stirring and under a trickle of dry air blanket, to 80°C for four hours to react the NCO groups of ingredient 6 to the OH groups of ingredients 4 and 5. Upon cooling to 50°C the following ingredients were added to the vessel with stirring:

- | | |
|-----------------------------|-----------|
| 7. Irgacure 184 (from Ciba) | 1.0 parts |
| 8. Benzophenone | 2.0 parts |
| 9. Silwet L7604 | 0.2 parts |

This composition had 64% oligomer and 36% reactive diluents, a NCO/OH of 0.933 and a hydroxyacrylate/polyol of 3.24. Viscosity at 25°C of the composition was 14,500 cps. Kept away from actinic light sources, it was stable at room temperature for more than 2 years. At 70°C, it remained in its liquid state for over a 6-month period.

The above composition was curtain coated 3-mil thick on a rigid vinyl clad composite tile base. The coating was UV-cured 2 passes under a pair of 200-watt per inch medium pressure mercury lamps at a belt speed which resulted in a total UV dose of 2.32 J/sq cm.

Two comparative compositions were prepared, curtain coated on a rigid vinyl clad composite tile base, and UV-cured with the same dose of energy as the composition of the present invention. The two comparative compositions are both used on commercial floor covering. Comparative Composition 1 was similar in composition to Example 1 of US Pat. No. 5,003,026. Comparative Composition 2 was similar in composition to Product B of US Pat. No. 4,421,782.

The composition of Example 1 of the present invention and the two comparative compositions were subject to the following performance evaluations:

(1) Stain Resistance: Sample specimens were exposed 24 hours to 6 household stains consist of ink, magic marker, hair dye, tincture of iodine, shoe polish, and driveway sealant. The specimens were then cleaned with

isopropyl alcohol, soap and water. Stain areas were determined by a colorimeter for LAB color changes before and after exposure to the stains. Colorimeter reading results were reported in ΔE . Higher ΔE indicated poorer staining resistance properties.

5 (2) Gloss Retention: This was an accelerated abrasion resistance test. Sample specimens were laid under a leather clad traffic wheel which traveled in a circular motion. The wheel itself rotated along its own axle. Abrasive soils were applied on top of the specimens while the wheel traveled in the circular motion on top of them. After 90 minute duration, the
10 specimens were determined for their retention of gloss with a gloss meter. Higher gloss retention indicated better abrasion resistance. The results of this test coordinate well with actual gloss loss of the product in the field.

 (3) Deep Scratch and Gouge Resistance: This was an accelerated test. The test was similar to the gloss retention test except the rotation of
15 the wheel along its axle is at a different speed from its travel in circular motion and a more abrasive mixture of soils was used. The outcomes of the test were rated against a control with known performance. A higher rating indicated a better scratch and gouge resistance property.

Table 2

20	<u>Example 1</u>	<u>Comparative 1</u>	<u>Comparative 2</u>
Stain resistance	110	260	210
Gloss retention	87	85	45
Gouge resistance	7	3	3

Example 2

25 The series of formulations in Table 3 were prepared, UV-cured, and tested as in Example 1. The results which are presented in the bottom of Table 3 showed that polyurethane acrylates, the reaction products of trifunctional isocyanates provided superior gloss retention, stain resistance, abrasion, scratch and gouge resistance.

Table 3

	Example	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
<u>Oligomer Reactants</u>					
(in % by weight)					
5	Desmodur N3390	--	--	--	--
	Desmodur N3300	30.30	35.78	19.58	28.71
	Polyol 1	8.97	8.34	21.81	6.91
	Polyol 2	--	--	--	--
	Tone M100	40.73	--	10.61	44.38
10	Placel FA1	--	35.88	--	--
<u>Reactive Diluents</u>					
(in % by weight)					
	SR351	--	--	--	--
	SR368	--	--	--	--
15	SR454	--	--	--	--
	SR499	--	--	24.00	--
	SR502	20.00	20.00	24.00	20.00
<u>Photoinitiators</u>					
(in phr)					
20	Benzophenone	2.00	2.00	2.00	2.00
	Irgacure 184	1.00	1.00	1.00	1.00
<u>Flow Aids</u>					
(in phr)					
	Silwet L7604	0.2	0.2	0.2	0.2
25	<u>Oligomer Equivalent Ratio</u>				
	NCO/OH	1.05	0.999	0.976	0.969
	Hydroxyacrylate				
	/polyol	4.0	5.67	0.43	5.6
<u>Comparative Properties</u>					
30	Stain				
	Resistance, ΔE	177	130	139	200
	Gloss				
	Retention, %	96	87	96	96
	Gouge Resistance	7	5	3	6

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Table 3 (Cont.)

	Example	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>
<u>Oligomer Reactants</u>					
(in % by weight)					
5	Desmodur N3390	--	--	--	--
	Desmodur N3300	17.54	27.45	22.03	17.54
	Polyol 1	22.32	--	8.87	22.31
	Polyol 2	--	13.8	--	--
	Tone M100	6.00	38.75	32.58	6.01
10	Placel FA1	--	--	--	--
<u>Reactive Diluents</u>					
(in % by weight)					
	SR351	--	--	10.00	--
	SR368	--	--	--	--
15	SR454	27.89	--	--	27.90
	SR499	26.25	20.00	13.00	--
	SR502	--	--	13.00	26.25
<u>Photoinitiators</u>					
(in phr)					
20	Benzophenone	2.00	2.00	2.00	2.00
	Irgacure 184	1.00	1.00	1.00	1.00
<u>Flow Aids</u>					
(in phr)					
	Silwet L7604	0.2	0.2	0.2	0.2
25	<u>Oligomer Equivalent Ratio</u>				
	NCO/OH	0.987	0.998	0.911	0.987
	Hydroxyacrylate				
	/polyol	0.24	4.0	3.24	0.24
<u>Comparative Properties</u>					
30	Stain				
	Resistance, ΔE	36	176	158	90
	Gloss				
	Retention, %	90	91	92	91
	Gouge Resistance	3	7	7	3

Desmodur N3300 is a trimer isocyanurate derived from hexamethyl diisocyanate. It has an equivalent weight of 195 and an average functionality of 3.5.

Desmodur N3390 is a 90% solid version of Desmodur N3300.

5 Placel FA1 has a molecular weight of 230.

Silwet L7604 is a silicone surfactant of OSi Specialties.

Example 3

The series of formulations in Table 4 were prepared, UV-cured, and tested as in Example 1. Examples N and O are comparative examples. The results
10 are presented at the bottom of Table 4. The results showed superior properties could be obtained from trifunctional isocyanate for the polyurethane acrylates for the present invention.

- 21 -
Table 4

Example	<u>I</u>	<u>J</u>	<u>K</u>	<u>L</u>	<u>M</u>	<u>N</u>	<u>O</u>
<u>Oligomer Reactants (in % by weight)</u>							
5	Desmodur N100	22.25	--	--	--	--	--
	Desmodur N3200	--	21.47	--	--	--	--
	Desmodur N3400	--	--	23.73	--	--	--
	Desmodur H	--	--	--	--	16.91	--
	Desmodur W	--	--	--	--	--	31.30
10	Polyisocyanate A	--	--	--	25.43	--	--
	Polyisocyanate B	--	--	--	--	23.57	--
	Polyol 1	8.93	9.10	14.90	8.75	8.61	--
	Polyol 3	--	--	--	--	--	11.94
	Tone M100	32.82	33.43	25.37	29.82	31.82	46.15
<u>Reactive Diluents (in % by weight)</u>							
15	SR351	10.00	10.00	16.00	14.00	16.00	--
	SR454	--	--	--	--	--	25.00
	SR499	13.00	13.00	10.00	10.00	10.00	--
	SR502	13.00	13.00	10.00	12.00	10.00	--
<u>Photoinitiators (in phr)</u>							
20	Benzophenone	2.00	2.00	2.00	2.00	2.00	2.00
	Irgacure 184	1.00	1.00	1.00	1.00	1.00	1.00
<u>Flow Aids (in phr)</u>							
	Silwet L7604	0.2	0.2	0.2	0.2	0.2	0.2
<u>Oligomer Equivalent Ratio</u>							
25	NCO/OH	0.933	0.934	1.000	1.000	1.091	1.000
	Hydroxyacrylate /polyol	3.24	3.24	1.50	3.00	3.26	2.00
<u>Comparative Properties</u>							
<u>Stain</u>							
30	Resistance, ΔE	210	213	138	194	95	231
<u>Gloss</u>							
	Retention, %	89	91	87	81	58	90
	Gouge Resistance	4	4	7	6	6	3

Desmodur N100 is a biuret isocyanate derived from hexamethylene diisocyanate. It has an equivalent weight of 191.

5 Desmodur N3200 is a biuret isocyanate derived from hexamethylene diisocyanate. It has an equivalent weight of 181.

Desmodur N3400 is a uretidione isocyanate. It has an equivalent weight of 193.

10 Polyisocyanate A is a mixture of polyisocyanates containing allophanate. It has an equivalent weight of 220.

Polyisocyanate B is a partial timer of methyl-bis(4-cyclohexylisocyanate). It has an equivalent weight of 178.7.

Claims:

1. A coating composition comprising a compound comprising structural units derivable from a polyisocyanate having at least two isocyanate functionalities per molecule, structural units derivable from a polyester polyol, and structural units derivable from a hydroxyalkyl(meth)acrylate having a molecular weight of about 116 to about 600.
2. A composition as claimed in claim 1, wherein the polyisocyanate has at least three isocyanate functionalities per molecule.
3. A composition as claimed in claim 1 or claim 2, wherein the polyester polyol is an aromatic polyester polyol.
4. A composition as claimed in any one of claims 1 to 3, wherein the hydroxyalkyl(meth)acrylate has an average molecular weight of about 344 to about 472.
5. A coating composition comprising the reaction product of a polyisocyanate having 3 to 6 isocyanate functionalities per molecule, an aromatic polyester polyol and a hydroxyalkyl(meth)acrylate with an average molecular weight of about 344 to about 472.

6. A composition as claimed in any one of claims 1 to 5, wherein the polyisocyanate is derived from three diisocyanate molecules.

7. A composition as claimed in any one of claims 1 to 6, wherein the polyisocyanate is selected from the group consisting of an isocyanurate, a biuret and an allophanate.

8. A composition as claimed in any one of claims 1 to 6, wherein the polyisocyanate is selected from the group consisting of those prepared from 1,6-hexamethylene diisocyanate; methylene-bis(4-cyclohexylisocyanate); 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; toluene diisocyanate; methylenediphenyl diisocyanate; tetra methylxylene diisocyanate; and mixtures thereof.

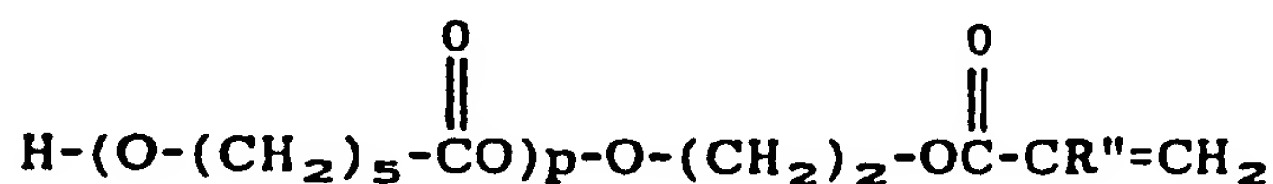
9. A composition as claimed in any one of claims 1 to 8, wherein the polyester polyol is a polyester polyol of acid number of less than 15 comprising the reaction product of an equivalent excess of one or more polyols of equivalent weight less than 150 with at least one of the group consisting of polycarboxylic acids and derivatives thereof, wherein at

least 50 equivalent percent of the polycarboxylic acid(s)/derivative(s) is selected from the group consisting of aromatic polycarboxylic acids, derivatives thereof, and mixtures of two or more substances selected from aromatic polycarboxylic acids and their derivatives.

10. A composition as claimed in claim 9, wherein the derivatives are selected from anhydrides and esters.

11. A composition as claimed in claim 9 or claim 10, wherein the aromatic polycarboxylic acid(s)/derivative(s) are selected from the group consisting of isophthalic acid, phthalic acid, terephthalic acid, phthalic anhydride, and dimethyl terephthalate.

12. A composition as claimed in any one of claims 1 to 11, wherein the hydroxyalkyl(meth)acrylate is a polycaprolactone-based hydroxy(meth)acrylate having the formula:



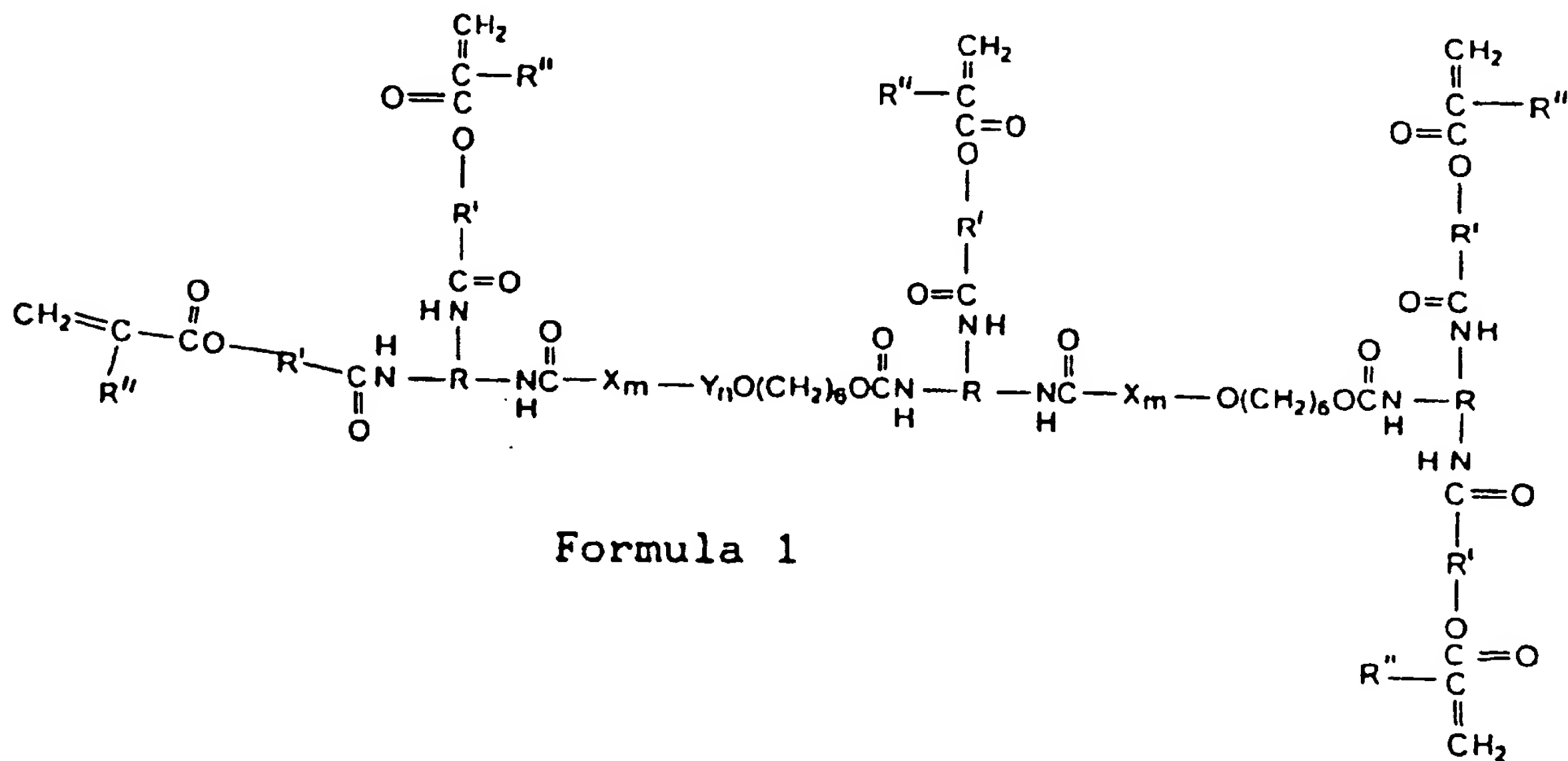
where $\text{R}'' = \text{H}$ or CH_3 , and

$p = 2$ or 3 .

13. A composition as claimed in claim 1 or claim 5, wherein the polyisocyanate is an isocyanate derived

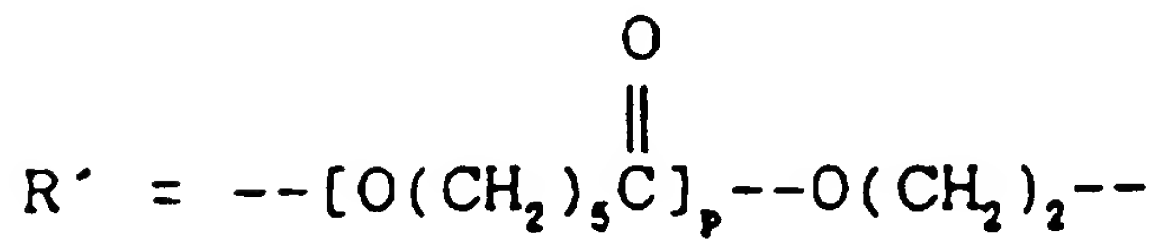
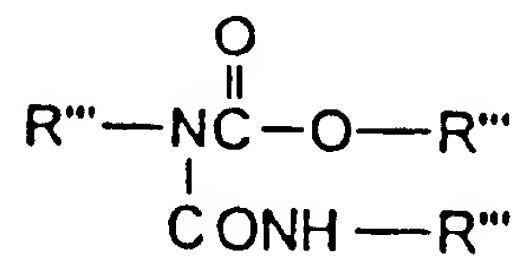
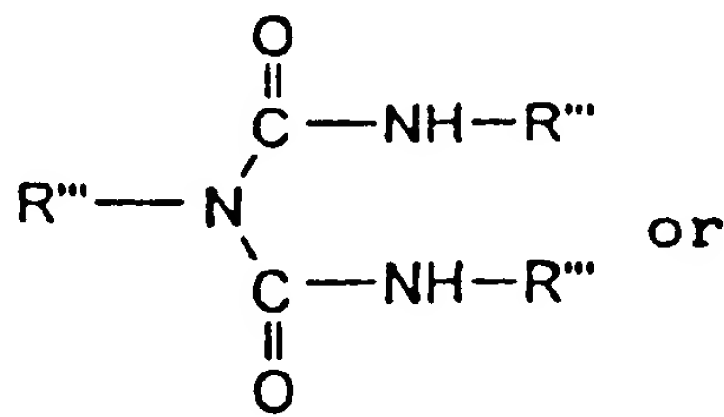
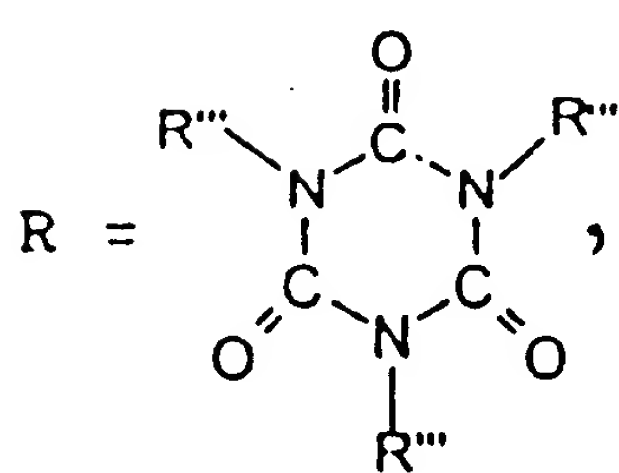
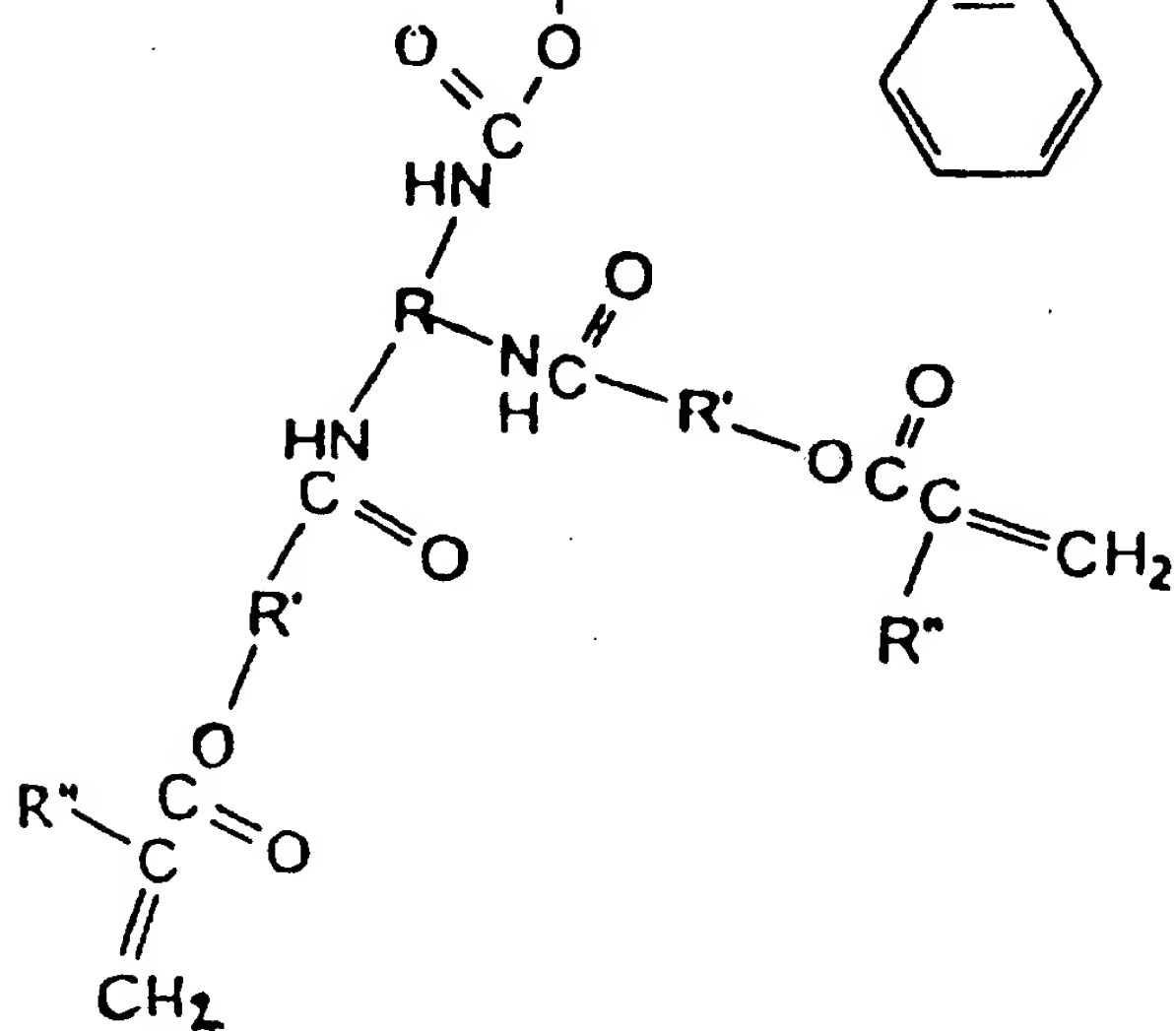
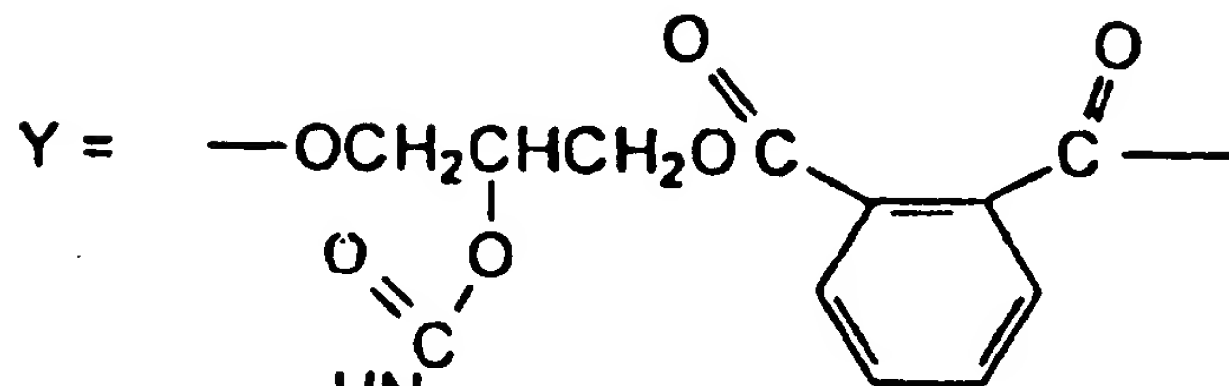
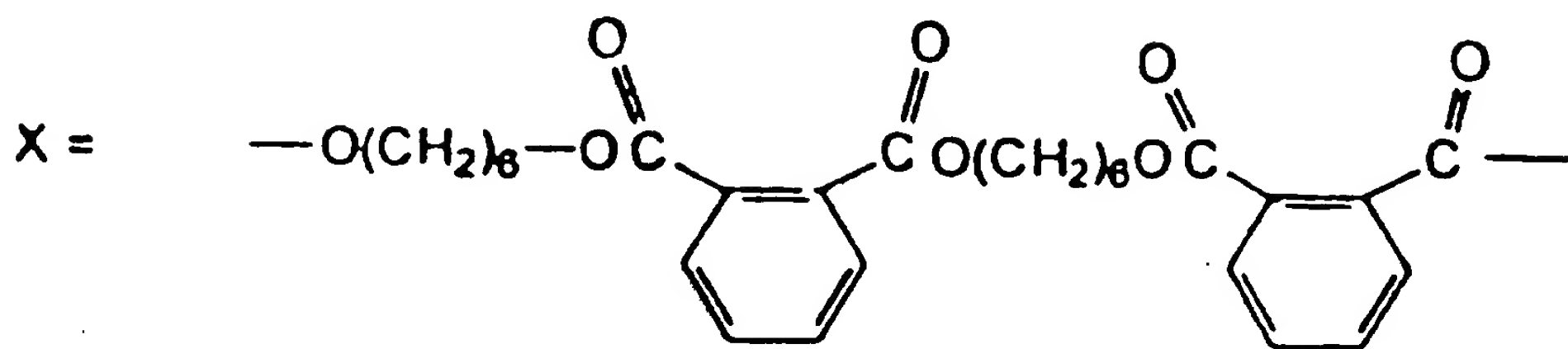
from hexamethyl diisocyanate, the polyester polyol is a phthalate polyester polyol wherein at least 50 equivalent percent of the polyol is 1,6-hexanediol and at least 50 equivalent percent of the polycarboxylic acid is phthalic acid or phthalatic anhydride, and the hydroxylalkyl(meth)acrylate is a polycaprolactone-based hydroxy(meth)acrylate having an average molecular weight of about 344, the isocyanate having an equivalent weight of about 195 and an average isocyanate functionality of about 3.5.

14. A coating composition comprising a multifunctional polyurethane(meth)acrylate having the following structure:



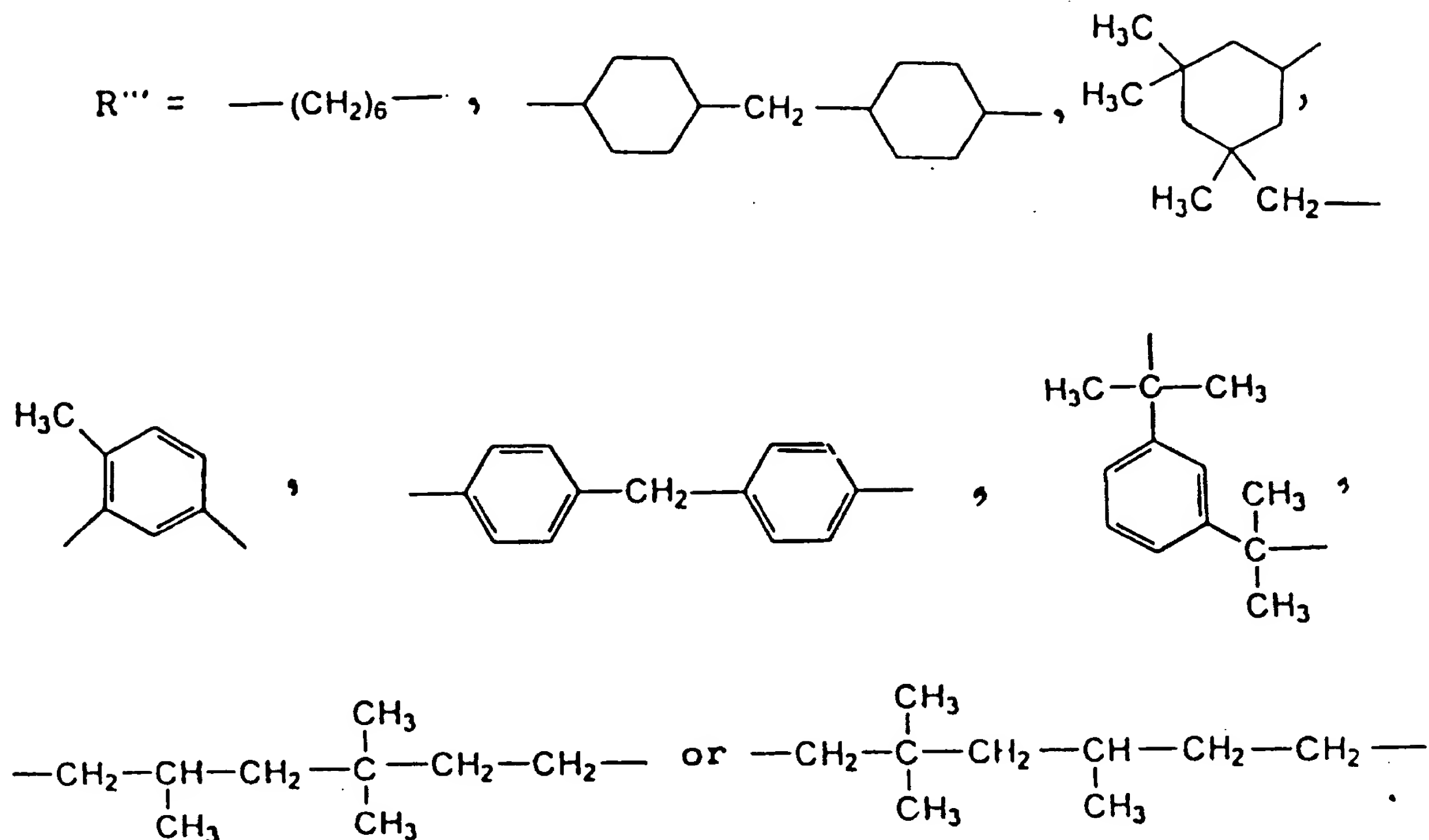
where $m = 0, 1$ or 2

$n = 1$



$p = 1, 2 \text{ or } 3$

$R'' = \text{H or CH}_3$



15. A composition as claimed in any one of claims 1 to 14, which also comprises a (meth)acrylate reactive diluent.

16. A composition as claimed in claim 15, wherein the diluent has a molecular weight of at least 200 and less than 2000.

17. A composition as claimed in claim 15 or claim 16, wherein the diluent is selected from the group consisting of ethoxylated tri(meth)acrylate and propoxylated tri(meth)acrylate.

18. A composition as claimed in claim 15 or claim 16, wherein the (meth)acrylate diluent is selected from the group consisting of tetraethylene glycol diacrylate, ethoxylated bisphenol-A diacrylate, trihydroxyethyl isocyanurate triacrylate, trimethylol propane triacrylate, and ethoxylated trimethylol propane triacrylate.

19. A composition as claimed in any one of claims 1 to 18, which also comprises a photoinitiator.

20. A coating composition as claimed in claim 1 and substantially as described in any one of the Examples herein.

21. A method of manufacturing a coated substrate, which comprises applying to a base layer a composition as claimed in any one of claims 1 to 20 and curing the composition.

22. A method as claimed in claim 21, carried out substantially as described herein.

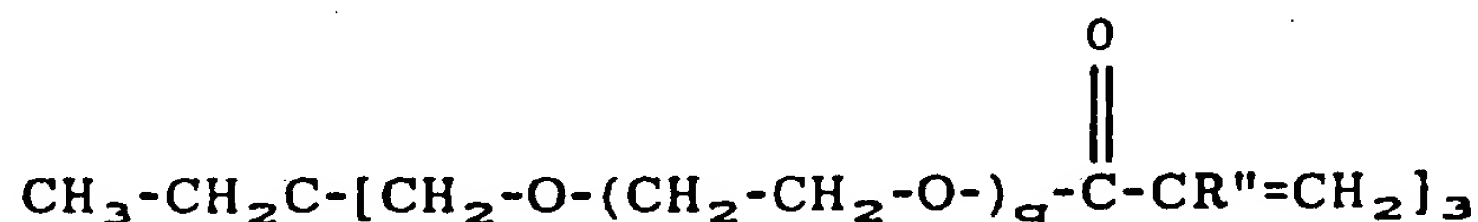
23. A coated substrate obtained by a method as claimed in claim 21 or claim 22.

24. A floor covering comprising a base layer and wear layer adhered to the base layer, the wear layer comprising a cured coating composition, the coating composition comprising a (meth)acrylate reactive diluent having a molecular weight of about 200 to about 2000 and the reaction product of a polyisocyanate with a functionality of 3 to 6 isocyanate functionalities per molecule, a polyester polyol, and a hydroxylalkyl(meth)acrylate with a molecular weight of about 344 to about 472.

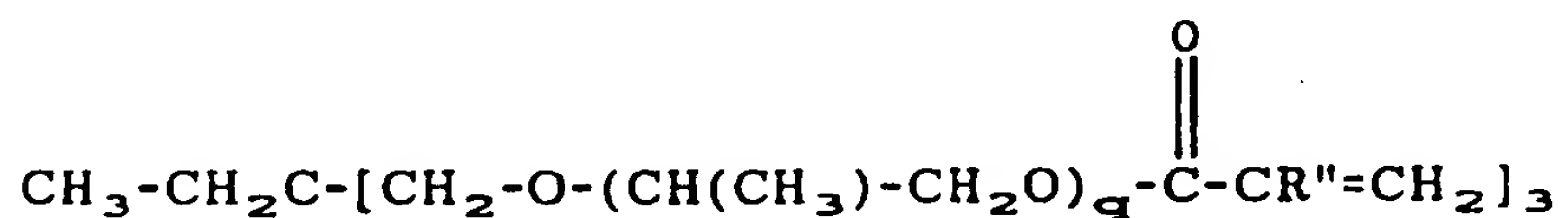
25. A floor covering as claimed in claim 24, wherein the (meth)acrylate diluent is selected from the group consisting of ethoxylated tri(meth)acrylate and propoxylated tri(meth)acrylate.

26. A floor covering as claimed in claim 24, wherein the (meth)acrylate diluent is selected from the group consisting of (meth)acrylic acid, isodecyl (meth)acrylate, N-vinyl formamide, isobornyl (meth)acrylate, tetraethylene glycol (meth)acrylate, tripropylene glycol (meth)acrylate, hexanediol di(meth)acrylate, ethoxylated bisphenol-A di(meth)acrylate, ethoxylated neopentyl glycol di(meth)acrylate, propoxylated neopentyl glycol di(meth)acrylate, ethoxylated tripropylene glycol di(meth)acrylate, glyceryl propoxylated

tri(meth)acrylate, tris (2-hydroxy ethyl) isocyanurate
tri(meth)acrylate, pentaerythritol tri(meth)acrylate,
pentaerythritol tetra(meth)acrylate, dimethylol propane
tri(meth)acrylate, dipentaerythritol monohydroxy-
penta(meth)acrylate, and trimethylol propane
tri(meth)acrylate and its ethoxylated and propoxylated
analogues of the structure selected from the group
consisting of



and



where $\text{R}'' = \text{H or CH}_3$, and

$q = 0, 1, 2, \dots, 9 \text{ or } 10$.

27. A floor covering as claimed in claim 26,
wherein the (meth)acrylate diluent is selected from the
group consisting of tetraethylene glycol diacrylate,
ethoxylated bisphenol-A diacrylate, trihydroxyethyl
isocyanurate triacrylate, trimethylol propane
triacrylate, and ethoxylated trimethylol propane
triacrylate.

28. A floor covering as claimed in any one of
claims 24 to 27, wherein the coating composition further

comprises a photoinitiator.

29. A coated substrate or floor covering as claimed in claim 23 or claim 24 and substantially as described herein.

30. A compound or reaction product as specified in any one of claims 1 to 14 and 24.

31. A method of making a compound or reaction product, which comprises reacting together a polyisocyanate having at least two isocyanate functionalities per molecule, a polyester polyol, and a hydroxyalkyl(meth)acrylate having a molecular weight of about 116 to about 600.

32. A method as claimed in claim 31, wherein one or more of the starting materials is as specified in any one of claims 2 to 13.

33. The product of a method as claimed in claim 31 or claim 32.

34. Any novel feature described herein, or any novel combination of herein described features.



Application No: GB 9625099.8
Claims searched: 1-33

Examiner: Alan Kerry
Date of search: 25 February 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.O): C3R RSX; C3P PDIE
Int CI (Ed.6): C08G 18/67; C09D 175/16
Other: Online database: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2022599 A (LORD) see Claims 1 & 9 and Examples	1, 3, 8-11, 15, 16, 19, 21-23, 31
X	EP 0394695 A2 (TOYO) see the Examples	1, 3, 8-11, 15, 16, 19, 21-23, 31
X	EP 0290623 A1 (NIPPON KAYAKU) see Claims 1 & 3 and the Examples	1, 8, 12, 15, 16, 19, 21-23, 31
X	US 4082634 (PPG) see Claims 1-4 and Examples 3-7	1, 3, 8-11, 15, 16, 19, 21-23, 31
X	WPI Abstract Accession No. 90-175294/23 & JP 02 115213	1, 2, 6-8, 31

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.